ATTACHMENT OF DONOR-ACCEPTOR STENHOUSE ADDUCTS PHOTOCHROMIC COMPOUNDS ONTO COTTON FABRICS

A Thesis

Presented to the Faculty of the Graduate School

of Cornell University

In Partial Fulfillment of the Requirements for the Degree of

Master of Science

by

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August 2017

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ABSTRACT

This thesis reported on the chemical attachment of a new photochromic organic molecule onto cotton fabrics. The photochromic molecule used in this study is a type of Donor-Acceptor Stenhouse Adducts (DASA) that switches color when exposed to visible light/heat. The attachment process included two steps: (1). Modification of cotton with N, N-methyl(2-bromo-ethyl) ammonium bromide to generate a secondary amine functionality in the cotton fabrics; and (2). Ring opening of the activated furfural in 5-(furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione by the modified cotton fabrics. These two steps allowed the formation of DASA molecules on the surface of the cotton fabric. The DASA-modified cotton fabrics can change color from pink to colorless when exposed to liquid water, and they return from colorless to pink when heated. This is the first time that this type of DASA molecule is immobilized onto a solid substrate without losing functionality. The modified fabrics can be used as sensors or made into clothes that can respond to visible light, water, and heat.

BIOGRAPHICAL SKETCH

Fangfang Weng was born in Zhejiang Province, China, and grew up in Wenzhou, a city of Zhejiang Province, China. She entered Donghua University to study Textile Design (Textile design) for three years. During her study at Donghua University, she was a member of Professor Yiping Qiu's research group working on the 3D woven fabric as filtration. In her senior year, she got the opportunity to study abroad at Cornell University, which was sponsored by China Scholarship Council. After graduation, she continued her master degree in fiber science and apparel design in Cornell University in the year of 2015.

As a graduate student in Cornell, Fangfang worked in Professor Juan Hinestroza's nanotextile lab. Instead of textile design, Fangfang pursue master degree in fiber science. With the help of her advisor and minor committee members, she conducted her research and completed her master thesis in the May of 2017.

ACKNOWLEDGMENTS

I would like to thank my advisor, Professor Juan Hinestroza, who helped me tremendously with my research and thesis writing. I would also like to express my gratitude to my minor committee members, Professor Denise Green, who has given me valuable feedback and advice based on her specialties and professional experience. I also appreciate Diego Alzate Sanchez, who taught me how to do chemistry synthesis and helped me build up the basic idea about chemistry. In addition, I want to thank Javier Jimneze, who worked together with me on my thesis. Lastly, I want to thank my family and friends who always stand on my side and give me love and encouragement.

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Chapter 1 Introduction

Centuries ago, when people talked about textiles, what came to mind was that clothes provide warmth and beauty. Since the development of machines and the industrial revolution, textiles have many industrial applications in addition to clothing. A new generation of textile technology is under way. The idea behind these innovations is to insert a variety of functions into a single fabric.

The challenge we face now is to functionalize textiles by making them sensitive to and responsive to the environment. In this thesis, a new type of modified cotton fabric will be introduced: it can change color according to visible light, water, and heat.

1.1. Photochromic molecules

Visible light is an ideal external stimulus to alter a molecular structure because it is readily available and costs nothing. Light is an environmentally friendly resource and will not contaminate samples. Thus, the scientific community is enthusiastic about working with photoswitches, which have unique properties and are relatively easy to work with. Photochromic properties can be used in surface patterning[1], photo robotic or micromechanics[2], naonoparticle clustering detection[3], control of biologically active molecules[4] and other applications.

Varieties of photochromic molecules have already been designed. The color switch relies on two types of geometric change. One is the structural switch between *cis* and *trans* isomers, among which azobenzenes is one of the most widely studied class. Light and heat in the dark can trigger the reversible transformation. **Fig. 1** shows the mechanism of photoisomerization of azobenzenes.

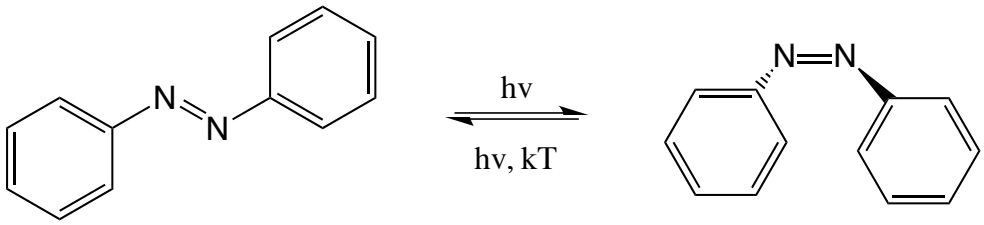


Figure 1 Mechanism of photoisomerization of azobenzenes

Another type of geometric change that is exploited by a color switch relies on interconversion between closed and open forms. Spiropyrans undergo this type of transformation. The photochromic behavior of spiropyrans is driven by the heterolytic cleavage of Cspiro−O bond upon UV irradiation (360−370 nm), resulting in the formation of a zwitterionic conjugated system. [5] This isomerization occurs together with a significant change in polarity. It is switchable both thermally and photochemically, by irradiation with visible (>460 nm) light.[6] **Figure 2** shows the mechanism of the photoisomerization of spiropyrans.

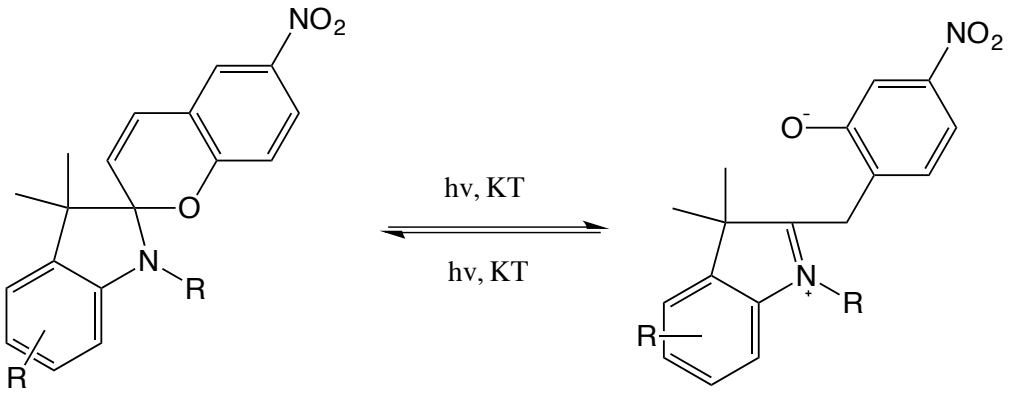


Figure 2 Mechanism of the photoisomerization of spiropyrans

In addition to azobenzenes and spiropyrans, other photochromic molecules are under extensive

study. Most of them have a reversible switch yield by UV/vis and heat. Some could have a polarity change accompanying the photoswitch.

1.2 What is DASA- Donor-Acceptor Stenhouse Adducts?

A Donor-Acceptor Stenhouse Adduct (DASA), is a type of newly developed organic photochromic compound. DASA molecules have an open structure, are intensely colored, and hydrophobic, but when entirely irradiated by visible light they cyclize to a colorless and hydrophilic zwitterionic structure. This new class of photoswitching molecules has many derivatives. The general structure is shown in **Figure 3**. A secondary amine group

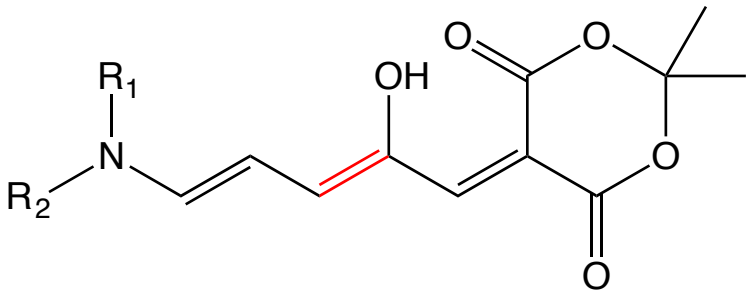


Figure 3 Basic structure of DASA molecules

works as "donors" (electron-rich), and the ring structure part is "acceptors"(electron-deficient) [7]

The starting materials to synthesize DASA derivatives are commercially accessible. In two steps, the product can be obtained with high yield.

The photoswitching behavior of DASAs has been proven to be reversible and highly resistant. However, the reversibility of color changes varies considerably in different organic solvents, which shares a similarity with spiropyran[8] and diarylethene[9] systems.

First generation dialky DASAs can convert into colorless zwitterionic cyclopentenone

form in protic solvents (methanol) irreversibly. In contrast, when in halogenated solvents (dichloromethane, chloroform, or chlorobenzene) thermal reversion to the colored triene occurs while photoisomerization does not. Reversibility of dialky DASAs only happens in aromatic solvents (toluene, benzene, or xylenes). [10]

Second generation aniline DASAs have had a great breakthrough on organic solvent selection. Photoswitching not only happens in non-polar aromatic solvents but also in polar solvents such as THF, DCM, ethyl acetate, and acetonitrile.[11]

1.3 Mechanism of DASA photoswitching

The photoswitching of DASA molecules belongs to interconversion between DASA's closed and open forms. See **Figure 4**. The specific change of the molecules during the process has been studied to unravel the potential of this new type of organic molecule. An actinic step is involved to switch DASA molecules from **A** to an intermediate **B**, which is a Z-E isomerization. Upon irradiation, **B** could be formed rapidly and reach a photostationary state under low temperature (253K). At higher temperature (293K), **B** undergoes thermal 4-πelectrocyclization and the proton transfer generates the closed ring structure **C**. [12] Thus, at room temperature, DASA molecules could change from a bright pink color to colorless with visible light.

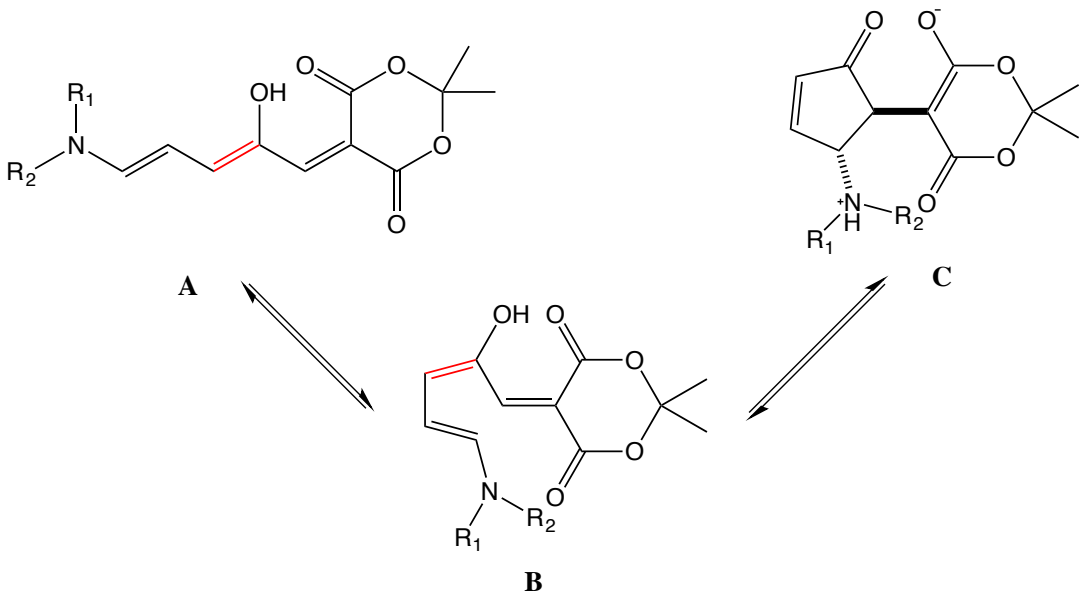


Figure 4 DASA molecules' photoswitching mechanism

1.4 DASA cotton:why?

The photoswitching property of DASA molecules enables application in many areas, such as chemical sensing[13], tracing of biological processes [14], and more. However, DASA molecules are explored in solution in the majority of the cases. Some research groups have DASA molecules combined with polymers, which is solid state chemistry. In this research, we involve one of the most common carriers, cotton, to accommodate DASA molecules. Here are the reasons why we use cotton.

First, cotton is the most widely used textile material and can be accessed everywhere. Thus, we can use the properties of the DASA molecules in a way that is closer to daily life than if our material were only accessible in a research situation.

Second, we can easily obtain cotton fabrics at a very reasonable price, thus reducing the cost of our raw materials.

Third, the main component of cotton is cellulose, which has a high potential for modification because of its reactive hydroxyl groups.

Another point to keep in mind is that the photoswitching happens under particular conditions. Solvents could play significant roles during the color change as mentioned before. Whether these properties remain the same after we attach DASA molecules on cotton needs to be explored.

Chapter 2 Methodology

At first glance, DASA molecules could be attached to cotton via etherification of hydroxyl groups on the cellulose molecule. However, this etherification is not possible, because most of the DASA molecules do not have functional groups that could react with cellulose. In order to overcome this situation, we decided to pursue a two-step approach as shown in **Figure 5**.

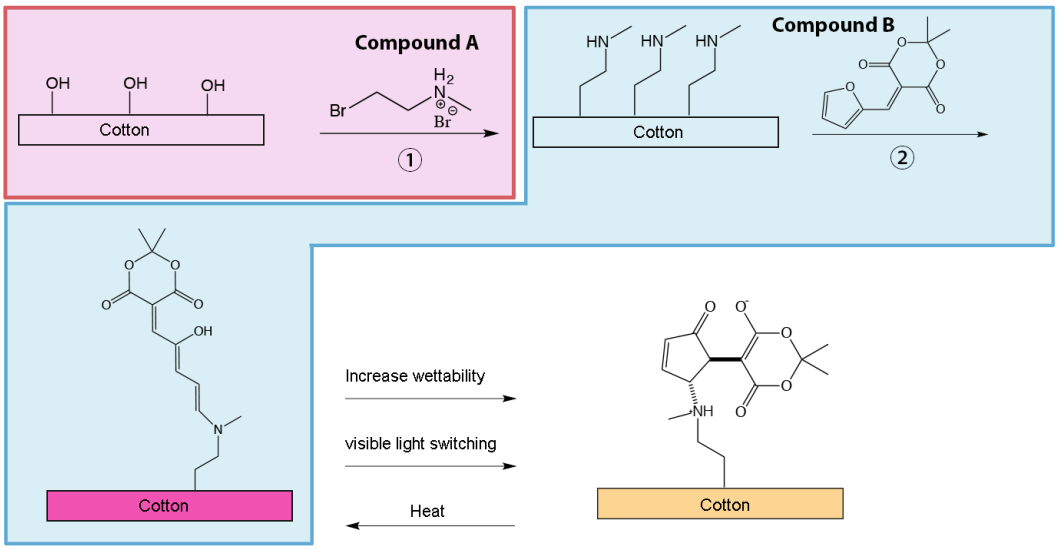


Figure 5 Proposed Mechanism of formation of DASA molecules on cotton

The first step in the proposed route is the synthesis of compound A (N, N-methyl(2-bromo-ethyl)ammonium bromide).

2.1 Synthesis of N, N-methyl(2-bromo-ethyl)ammonium bromide

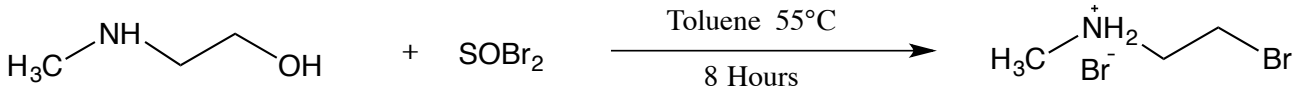


Figure 6 Synthesis of N,N-methyl(2-bromo-ethyl)ammonium bromide

1.2ml of 2- (methylamino)ethanol was added dropwise to a flask containing 10 ml of toluene. Then, 2.4ml of thionyl bromide was added to the flask. Significant heat was released upon the addition of thionyl bromide and the solution in the flask turned orange in color. The orange solution was stirred at 50°C for 8 hours. After 8 hours, we noticed two phases: an upper layer composed of toluene and a lower orange sticky layer. The lower layer was extracted using a separatory funnel. The unreacted thionyl bromide present in the lower layer was washed off with toluene. After 5 washes, the lower layer exhibited a light yellow color. The purified lower layer was added dropwise under continuous stirring into 100ml of cold acetone. The resulting colorless solution was placed in a fridge for 24 hours, during which white crystals were formed. [15]The white crystals (compound A) were collected and washed with cold acetone. H^1 NMR was used to confirm the structure of compound A as N, N-methyl(2-bromo-ethyl)ammonium bromide(**Figure 7**).

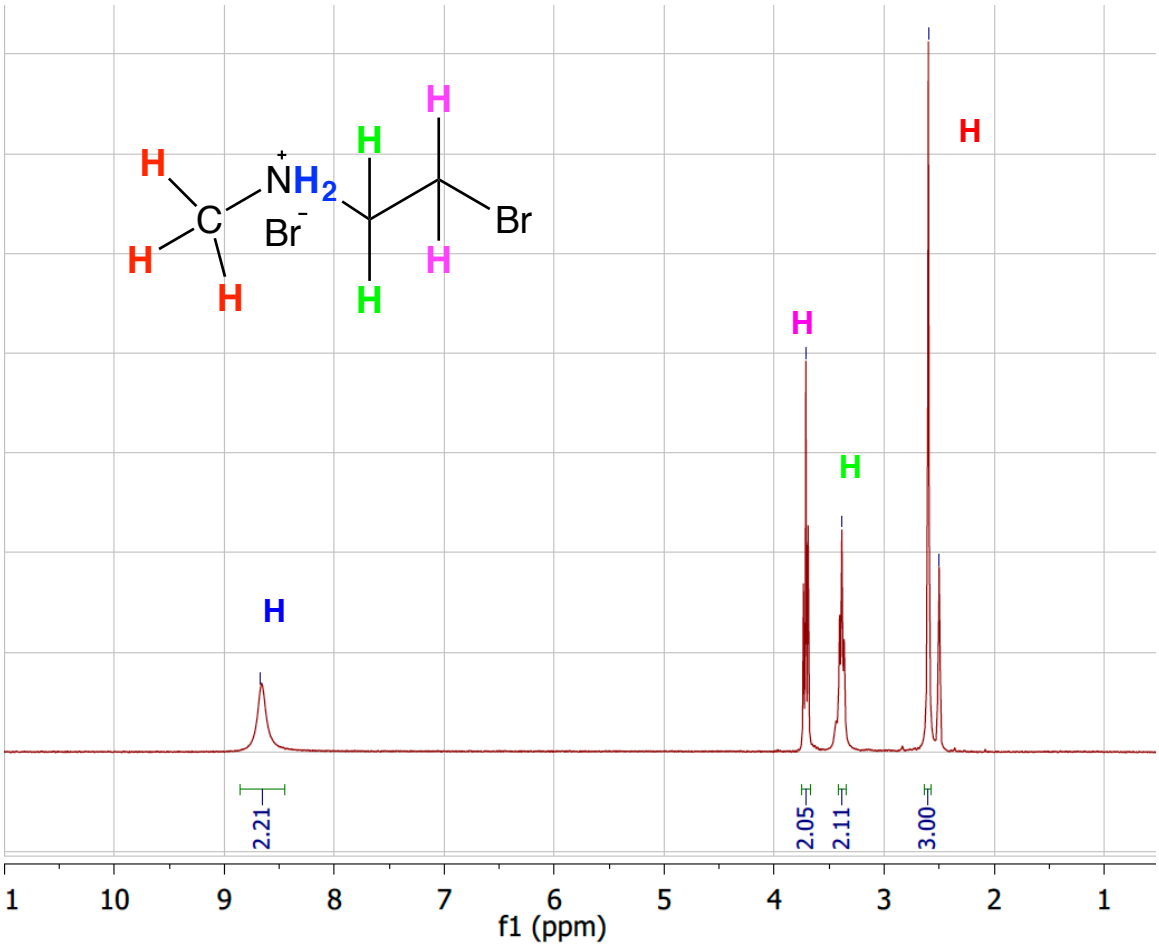


Figure 7 . H^1 NMR of N, N-methyl(2-bromo-ethyl)ammonium bromide

2.2 Synthesis of 5-(furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione

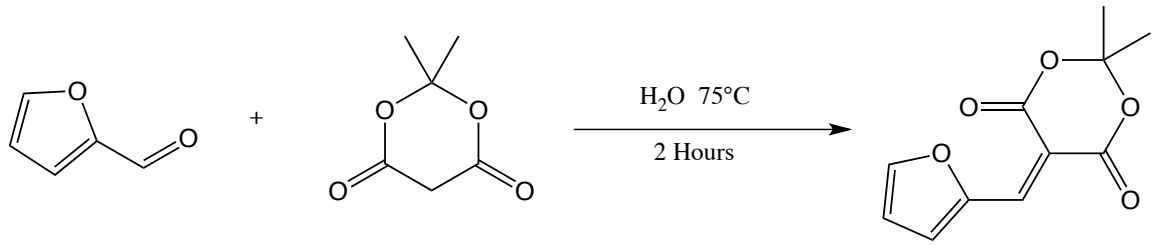


Figure 8 Synthesis of 5-(furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione

2, 2-dimethyl-1,3-dioxane-4,6-dione (1.51 g, 10.5 mmol) and 2-furaldehyde (961 mg, 10 mmol) were added to 30 mL of water. The mixture was under continuous stirring at 75 ^{O}C for 2 h, during which a dark green precipitate formed, and the solution was cooled down to room temperature. The precipitated solid was collected via vacuum filtration and washed twice with cold water. The dark green solid was dissolved in dichloromethane and the resulting solution became bright yellow in color, and some black solid precipitated. The solution was washed sequentially with (a).30 mL of saturated aqueous $NaHSO_3$, (b). 30 mL of water, (c) 30 mL of saturated aqueous $NaHCO_3$, and (d) 30 mL of saturated NaCl. The remaining solid impurities were filtered and a clear bright yellow organic layer was obtained. $MgSO_4$ was added to the organic layer to extract the remaining water. Dichloromethane solvent was removed using rotary evaporation yielding a yellow powder (compound B). [16] H^1 NMR was used to confirm the structure of compound B: 5-(furan-2-ylmethylene)-2,2-dimethyl- 1,3-dioxane-4,6-dione (**Figure 9**).

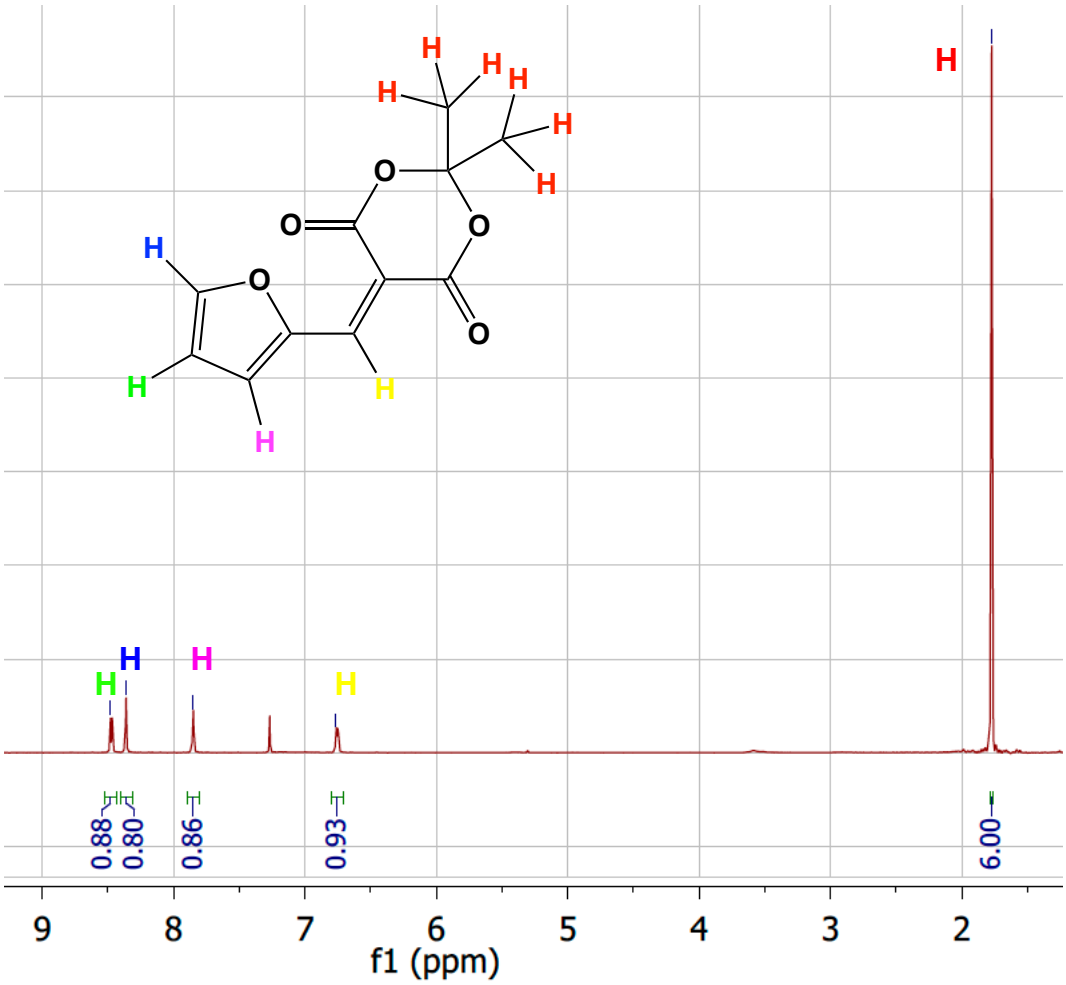


Figure 9 H^1 NMR of 5-(furan-2-ylmethylene)-2,2-dimethyl- 1,3-dioxane-4,6-dione

2.3 Step 1: reaction of N,N-methyl(2-bromo-ethyl)ammonium bromide and cotton

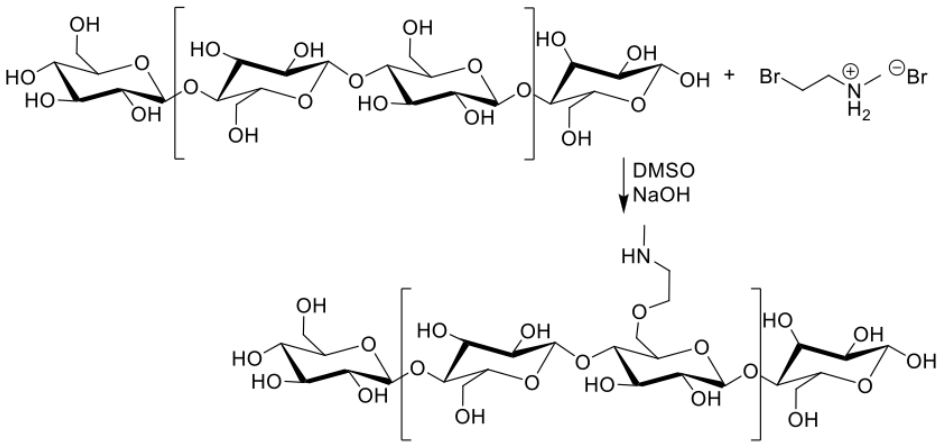


Figure 10 reaction of N,N-methyl(2-bromo-ethyl)ammonium bromide and cotton

40mg of powdered sodium hydroxide were added to a flask containing 5.6ml of dimethyl sulfoxide. A piece of cotton fabric (approximate 60mg) was added into the flask, and stirred at 65°C under nitrogen for 1 hour. After 1 hour, the cotton fabric inside the flask became light yellow. N, N-methyl(2-bromo-ethyl)ammonium bromide(217mg,1mmol) was added to the flask. The air in the flask was vacuumed out and replaced with nitrogen 3 times. The flask was heated at 65°C for 6 hours and the solution became brown in color. The cotton fabric was removed from the flask, washed with DMSO and methanol (3 times respectively), and dried in an oven at 65°C.

2.4 Step 2: assembly of the DASA molecules on cotton

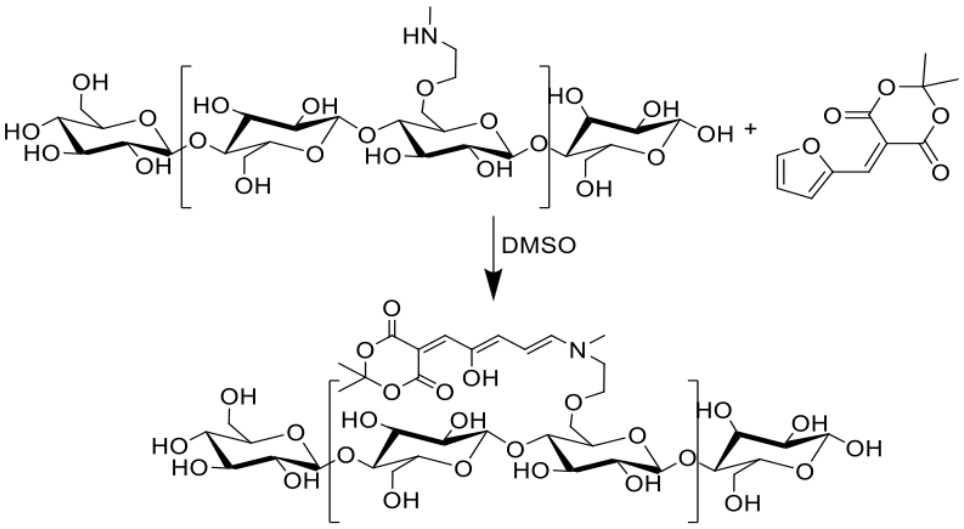


Figure 11 Assembly of the DASA molecules on cotton

5-(furan-2-ylmethylene)-2, 2-dimethyl-1,3-dioxane-4,6-dione(222mg,1mmol) was dissolved in 10 ml of dimethyl sulfoxide. The cotton fabric modified by N, N-methyl(2-bromo-ethyl)ammonium bromide was added into the solution and stirred for 4 hours at room temperature. After the reaction, the cotton fabric turned pink in color. Then the cotton fabric was washed with DMSO and methanol (3 times respectively) and dried in an oven at 65°C.

2.5 Controlled experiments

In order to optimize the attachment of DASA molecules to the cotton fabrics, controlled experiments were done to understand the effect of: (a). pretreatment of fabric, (b).

temperature of the reaction, (c). ratio of bromine to OH groups, and (d). time of the reaction.

2.5.1 Effect of Pre-treatment

Samples 1.1 to 1.5 were used to understand the effect of the fabric pretreatment. Sample 1.1 was the control-sample and was not subject to NaOH pretreatment. Samples 1.2 to 1.5 were subject to NaOH pretreatment at temperatures ranging from 25°C to 85 °C. All samples had a reaction time for 6 hours, a ratio of bromine to OH of 1:1 and a temperature of step1 reaction of 65°C.

Figure 12 contains the digital pictures of the specimens, the reflectance measurements as function of wavelength and color strength determination for each sample.

Digital photographs indicate that the color of sample 1.1 remains unaltered while sample 1.2 to 1.5 exhibit pinkish color at various degrees of intensity. The strength of the color was calculated using the reflectance measurements. Sample 1.3 and Sample 1.4 had very low reflectance and corresponding high color strength. Sample 1.2 exhibits the highest reflectance values and a corresponding color strength of 0.2455 ± 0.0358.

These results indicate that NaOH pretreatment is a requirement for activating the hydroxyl groups on cellulose, hence, enabling their reaction with the bromine group of compound A. Furthermore, the results indicate that the temperature of the pretreatment is an important factor. The temperature of pretreatment appears to affect the amount of the hydroxyl groups able to react with compound A. However, when temperature is above 65°

C, the color strength remained the same, which indicated that the saturation of activated hydroxyl groups.

Sample	Pre-treatment	Temperature of pre-treatment(°C)	Time of reaction(hr)	Br/OH	Temperature of reaction (°C)
1.1	none	65	6	1:1	65
1.2	NaOH	25			
1.3	NaOH	45			
1.4	NaOH	65			
1.5	NaOH	85			

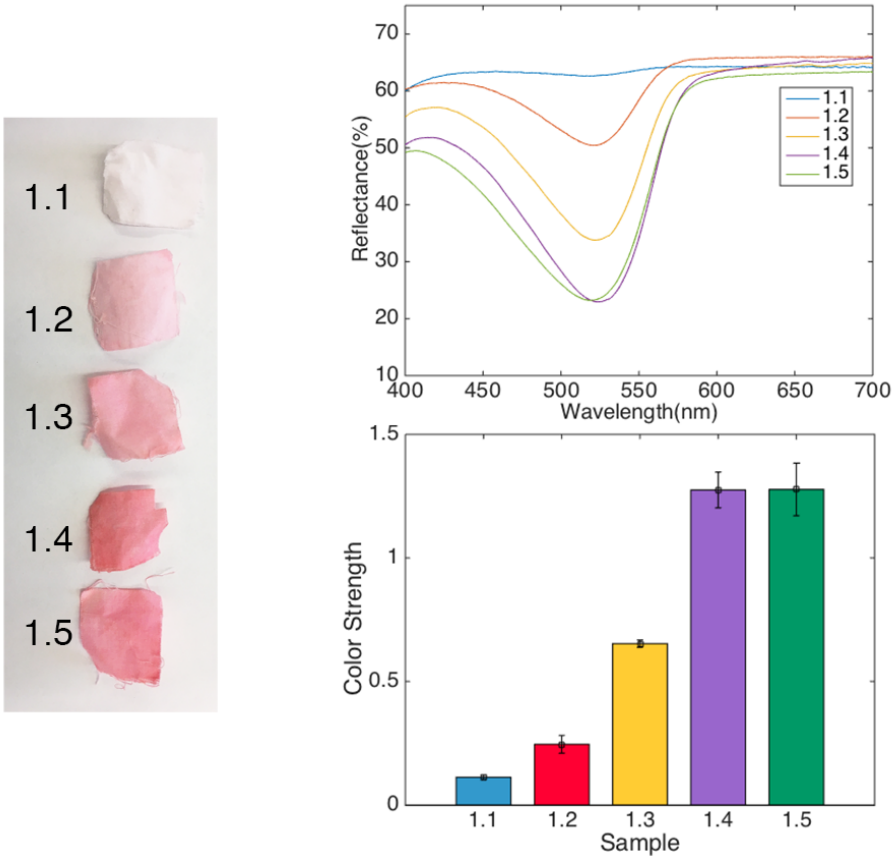


Figure 12 Digital pictures of the specimens, the reflectance measurements as function of wavelength and color strength determination for each sample with different pretreatment

2.5.2 Reaction temperature

Samples 2.1 to 2.4 were used to understand the effect of the reaction temperature.

Samples 2.1 to 2.4 reacted with compound A at temperatures ranging from 25°C to 85 °C.

All samples had a pretreatment with NaOH at 65°C, a reaction time for 6 hours, a ratio of bromine to OH of 1:1.

Figure 13 contains the digital pictures of the specimens, the reflectance measurements as function of wavelength and color strength determination for each sample.

Sample 2.1 to 2.4 exhibit pinkish color at various degrees of intensity. Sample 2.3 exhibits the lowest reflectance values and a corresponding color strength of 1.2749 ± 0.0724. Sample 2.1 exhibits the highest reflectance values and a corresponding color strength of 0.3282 ± 0.02.

These results indicate that a higher temperature enables more activated hydroxyl groups to react with the bromine groups of compound A. However, at the highest temperature 85°C, the intensity of pink color decreases to 0.7316±0.0564. This decrease may be caused by the degradation of compound A.

Fig 14 shows the TGA thermogram curve at 10 °C per minute of N, N-methyl(2-bromo-ethyl)ammonium bromide. It can be observed that reagent could have degradation at 85°C. The reaction of Sample 2.4 was conducted at 85° C for 6 hours, and the reagent could have degraded during that reaction leading to a lower attachment yield.

Sample	Pre-treatment	Temperature of pre-treatment(°C)	Time of reaction(hr)	Br/OH	Temperature of reaction (°C)
2.1 2.2 2.3 2.4	NaOH	65	6	1:1	25 45 65 85

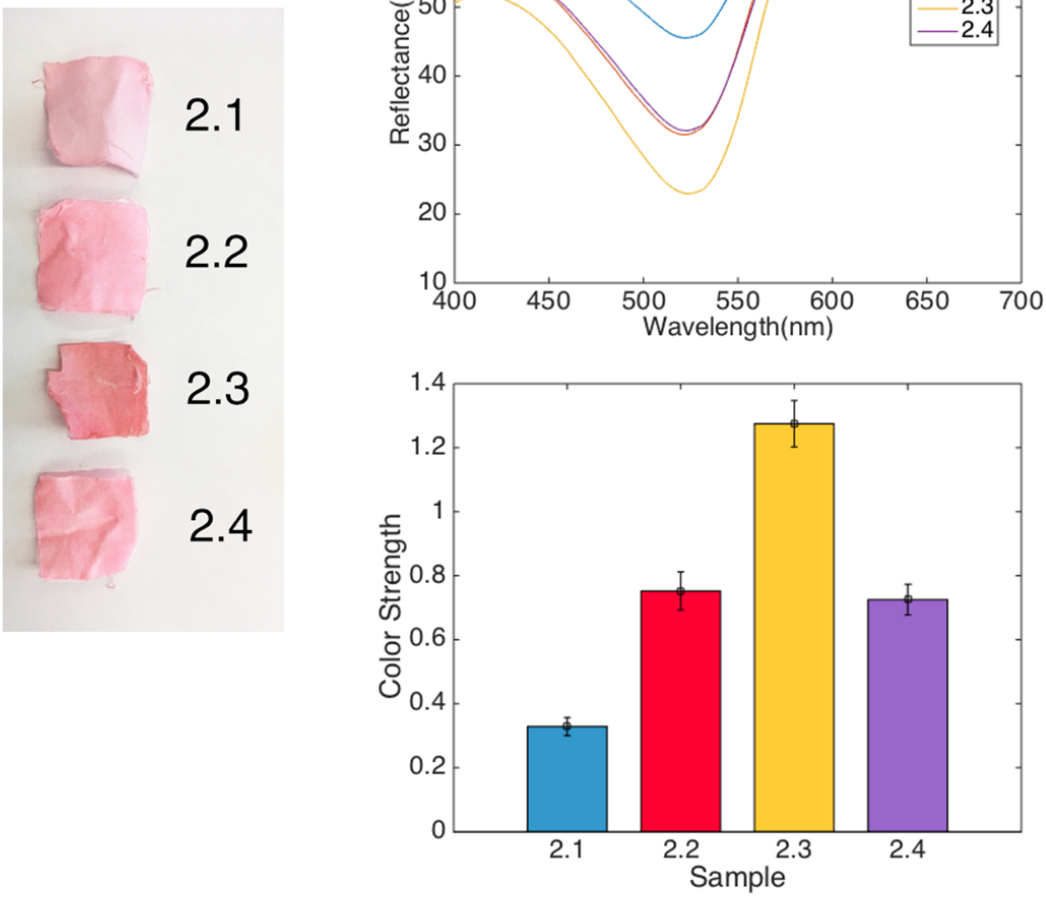


Figure 13 digital pictures of the specimens, the reflectance measurements as function of wavelength and color strength determination for each sample with different reaction temperature

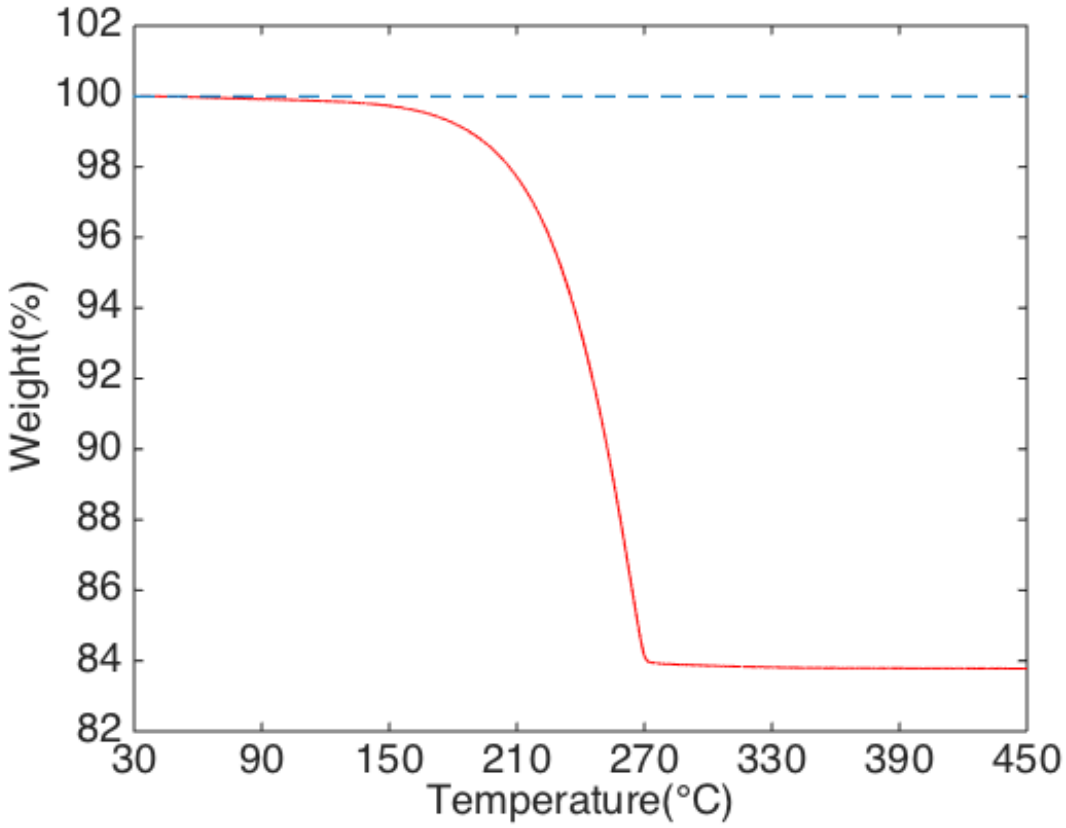


Figure 14 TGA test for N, N-methyl(2-bromo-ethyl)ammonium bromide

2.5.3 Molar ratio of compound A to hydroxyl groups on cotton

200mg cotton fabrics were used in each batch. In general, the cellulose content of cotton fiber is 90%.[17] The hydroxyl groups in cellulose are 18mmol/g. The calculation of the amount of N,N-methyl(2-bromo-ethyl)ammonium bromide we use is shown below:

$m_{cellulose}$ =200mg×90%=180mg

n_{OH}=18mmol/g×180mg=3.24mmol

Mass of the N,N-methyl(2-bromo-ethyl)ammonium bromide for 1:1 ratio:

m1=3.24mmol×217g/mol=703.08mg

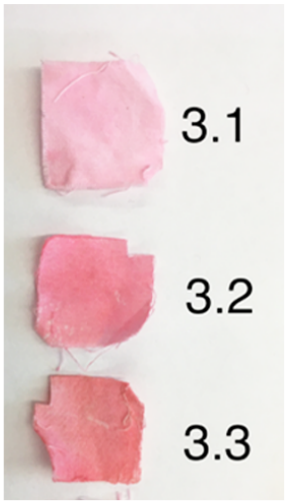
Samples 3.1 to 3.3 were used to understand the effect of the ratio of compound A to hydroxyl group on cotton. Samples 3.1 to 3.3 reacted with compound A at a ratio varying from 1:4 to 1:1. All samples had a pretreatment with NaOH at 65°C, a reaction time of 6 hours and a reaction temperature of 65°C.

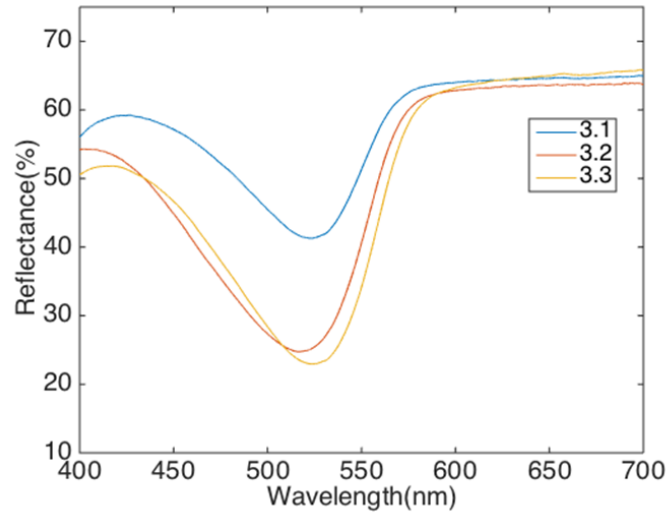
Figure 15 contains the digital pictures of the specimens, the reflectance measurements as function of wavelength and color strength determination for each sample.

Sample 3.1 to 3.3 exhibit pinkish color at various degrees of intensity. Sample 3.3 exhibits the lowest reflectance values and a corresponding color strength of 1.2749 ± 0.0724. Sample 3.1 exhibits the highest reflectance values and a corresponding color strength of 0.4195 ± 0.0129. Sample 3.2 shows a very close color strength to sample 3.3 within standard deviation.

These results indicate that a higher molar ratio of compound A to hydroxyl groups enables higher extent of the reaction. However, there is a limitation for activated hydroxyl groups on cellulose to react with compound A, upon which no further etherification could occur.

Sample	Pre-treatment	Temperature of pre-treatment(°C)	Time of reaction(hr)	Br/OH	Temperature of reaction (°C)
3.1 3.2 3.3	NaOH	65	6	1:4 1:2 1:1	65





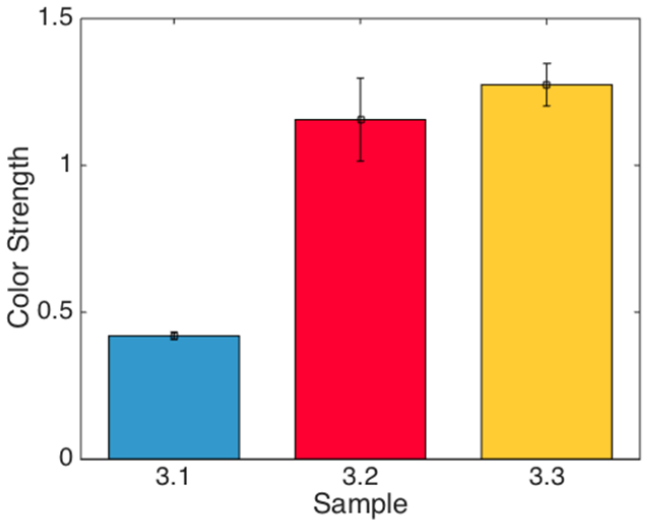


Figure 15 Digital pictures of the specimens, the reflectance measurements as function of wavelength and color strength determination for each sample with different Br/OH ratio

2.5.4 Time of reaction

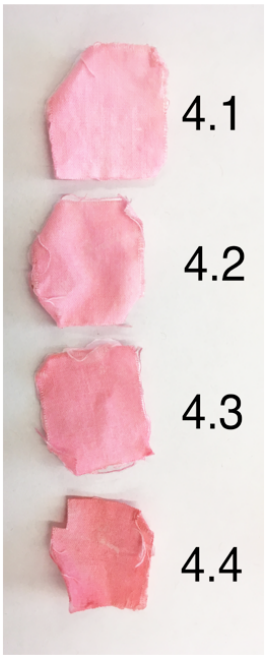
Samples 4.1 to 4.4 were used to understand the effect of the reaction time and find out the shortest time to reach the equilibrant of the reaction. Samples 4.1 to 4.4 reacted with compound A with time ranging from 1 hour to 6 hours. All samples had a pretreatment with NaOH at 65°C, a reaction temperature of 65°C, and a molar ratio of bromine to OH of 1:1.

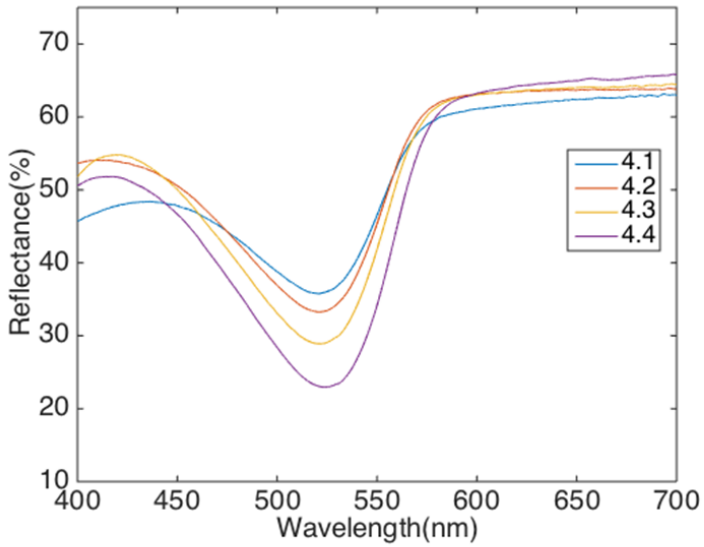
Figure 16 contains the digital pictures of the specimens, the reflectance measurements as function of wavelength and color strength determination for each sample.

Sample 4.1 to 4.4 exhibit pinkish color at various degrees of intensity. Sample 4.4 exhibits the lowest reflectance values and a corresponding color strength of 1.2749 ± 0.0724. Sample 2.1 exhibits the highest reflectance values and a corresponding color strength of 0.5774 ± 0.0265.

These results indicate that at least 6 hours reaction is needed in order to get intense color and higher degree of etherification. We performed experiments reaction times longer than 6 hours, but they resulted in physical damages of the samples.

Sample	Pre-treatment	Temperature of pre-treatment(°C)	Time of reaction(hr)	Br/OH	Temperature of reaction (°C)
4.1 4.2 4.3 4.4	NaOH	65	1 2 4 6	1:1	65





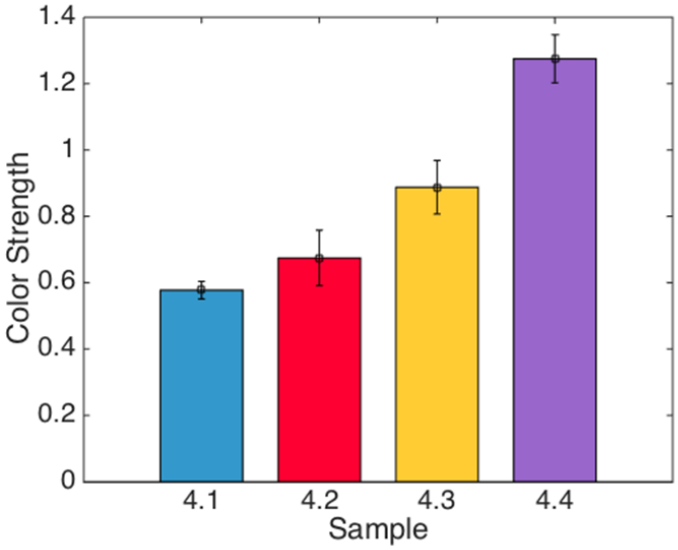


Figure 16 Digital pictures of the specimens, the reflectance measurements as function of wavelength and color strength determination for each sample with different reaction time

The reported results show that a pretreatment of NaOH is a must for attaching compound A on cotton, which provides an alkaline environment for etherification. With higher temperature, more hydroxyl groups could be activated by NaOH and more compound A could react those hydroxyl groups. However, the reaction temperature should not be above 75°C, which would cause the degradation of compound A and lower the degree of etherification. A higher ratio of compound A to hydroxyl groups could increase degree of attachment, however, there is a limitation upon which the attachment is saturated. At least 6 hours are needed to have a higher degree of etherification and get more intense color.

2.6 Properties of cotton fabrics modified with DASA

The cotton fabrics modified with DASA molecules appeared to be pink in color**.** This type DASA molecule could respond to visible light at certain solution, and switch color from pink to colorless. (reference) However, the photoswitching of DASA molecules is solvent selective. Thus, it is important to find out whether the attachment could affect the photoswitching mechanism of DASA.

2.6.1 Color switching under visible light

An array of white LED lights (with full wavelength of visible light) was focused on a cotton fabric modified with DASA (Sample A). Another cotton fabric modified with DASA (Sample B) was kept in the iron box to create complete dark environment. The color of Sample A was photographed every 5 minutes and it became colorless in 1 hour. Sample B was kept in the dark also became colorless after 1 hour, which indicated that visible light is not the only stimulus that triggered change of color of cotton fabrics

modified with DASA. Both Sample A and Sample B recovered the colors after they were heated in an oven at 65°C.

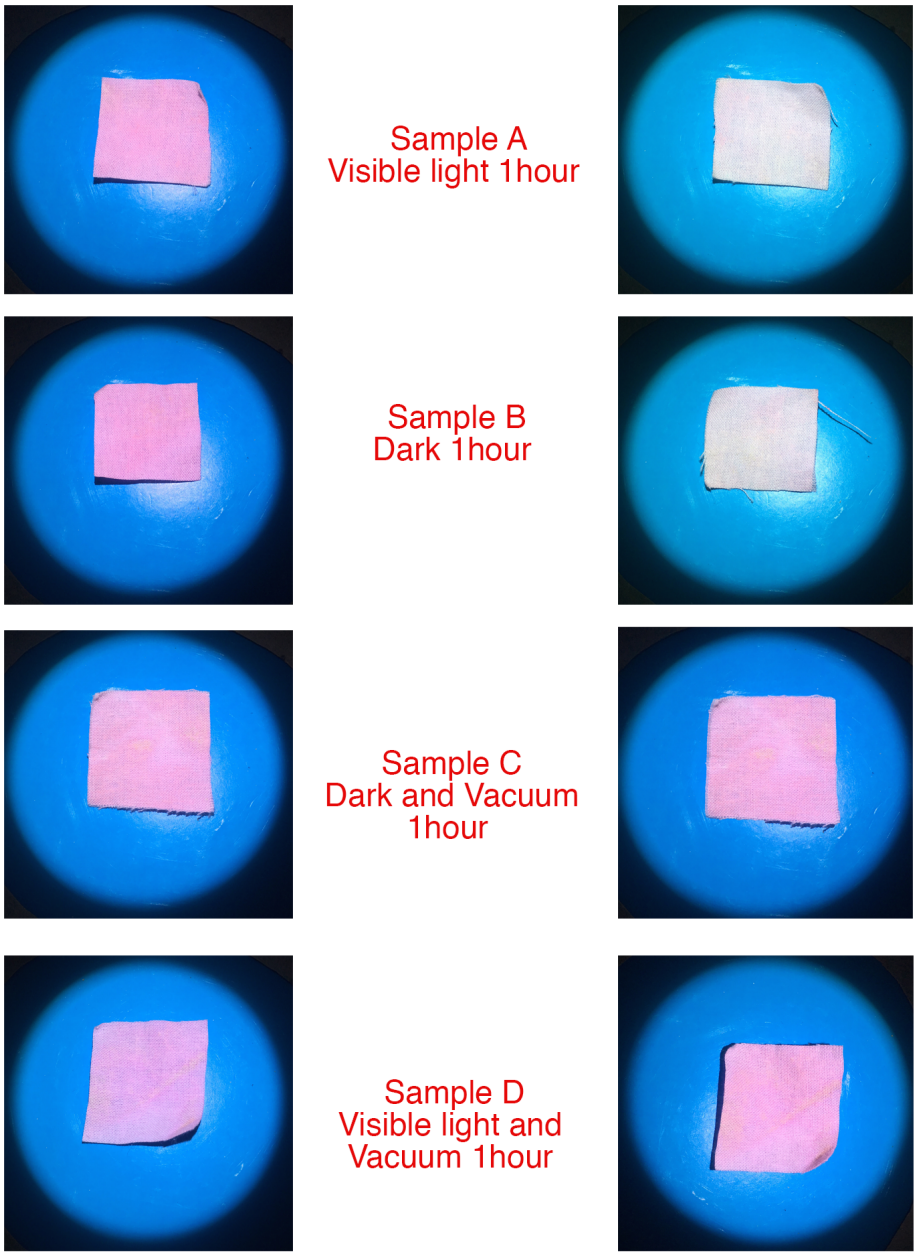


Figure 17 Color change of cotton fabric samples: A. under visible light, B. dark, C. dark and vacuum, D. visible light and vacuum

The possible reason for the color switch could be the moisture regain of cotton. A cotton fabric modified with DASA(Sample C) was put in a dark vial under vacuum and another cotton fabric modified with DASA(Sample D) was put under visible light under vacuum to confirm the proposed assumption. After 1 hour, the color of Sample C and Sample D remained unchanged. This experiment indicates that moisture regain plays the main role in the color change of Sample B.

2.6.2 Water induced color change

In an earlier study, Sameh Helmy[7] reported that the DASA molecule was insoluble in water, but after irradiation with visible light the compacted structure of DASA became hydrophilic, and water accelerated photoswitch. Our experiments also showed the moisture influence the color change of cotton fabrics modified with DASA. When water was dropped on the cotton fabric modified with DASA, the color changed immediately from pink to pinkish yellow. After drying the wet fabric with a paper towel, the fabric became colorless as shown in **Figure18**.

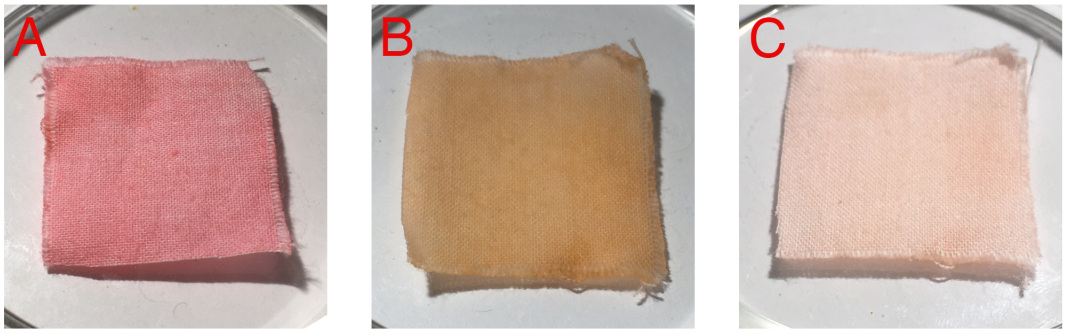


Figure 18 A. cotton fabric modified with DASA, B. Wet cotton fabric modified with DASA C. Colorless cotton fabric modified with DASA

The reversibility of color switch is also an important property need to be explored. The colorless cotton fabrics modified with DASA molecules was placed in an oven at 65°C. The color of the sample was photographed every 5 minutes as shown in **Figure 19.** We noticed that after 30 minutes heating, the color recovered.

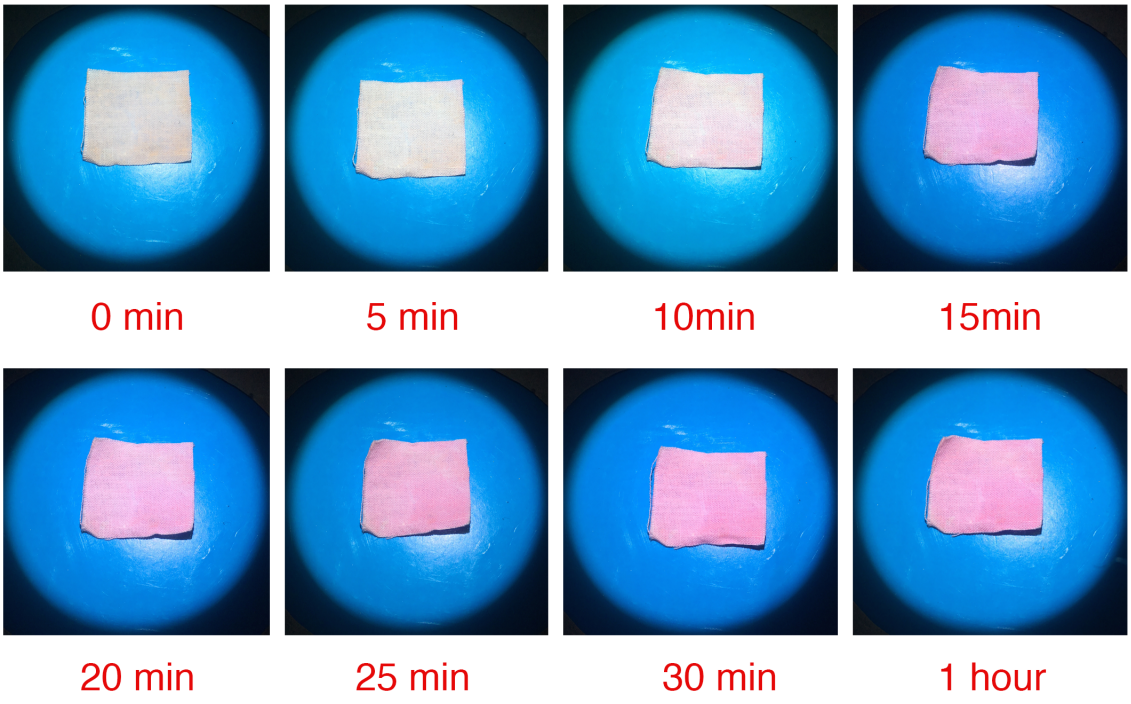


Figure 19 Color recovery of DASA cotton from colorless to colored at 65° C

2.7 Reflectance measurements

The interaction between the source of illumination and the objects contribute to the color appearance of the object. Within 400-700 nm range, the object selectively absorbs or reflects light of specific wavelength. 100% of the reflectance of the light indicates the surface reflects all the light striking on it, and appears to be white. Also, this surface reflect equal amount of the color at every wavelength. Most of the surface can be describe as colorful reflect light at selected wavelengths. For textile materials, wavelength reflections spectra can be used to interpret the color.[18]

Color strength could be expressed by a numerical value according to the amount of color absorbed by the specimen. In reflectance measurements, there are four commonly used types of calculation: SWL, SUM, WSUM and TSVSTR. In this case, SWL is used to calculate the strength at wavelength of maximum absorbance. K/S values could be calculated by the following equation[19]:

$$K/S=(1-R_\lambda)^2/(2\ R_\lambda)$$

Where:

R_λ is the reflectance at λ wavelength.

A Shimadzu UV-Vis-NIR spectrometer was used to measure the reflectance of the fabrics. Reflectance was measured at wavelengths from 400-700 nm with a 5 nm slit width. An untreated cotton fabric was measured as a reference group. **Figure 20** illustrates the reflectance of untreated cotton fabrics, cotton fabrics modified with DASA and colorless cotton fabrics. The untreated cotton fabric has very linear spectra while cotton fabrics

modified with DASA exhibits a significant drop between 425nm and 575nm with a minimum lowest peak at 523.8 nm. The colorless DASA cotton has a reduced reflectance between 425nm and 575nm. In conclusion, the color strength of colorless fabric is lower than the cotton fabric modified with DASA, but higher than the untreated cotton fabric.

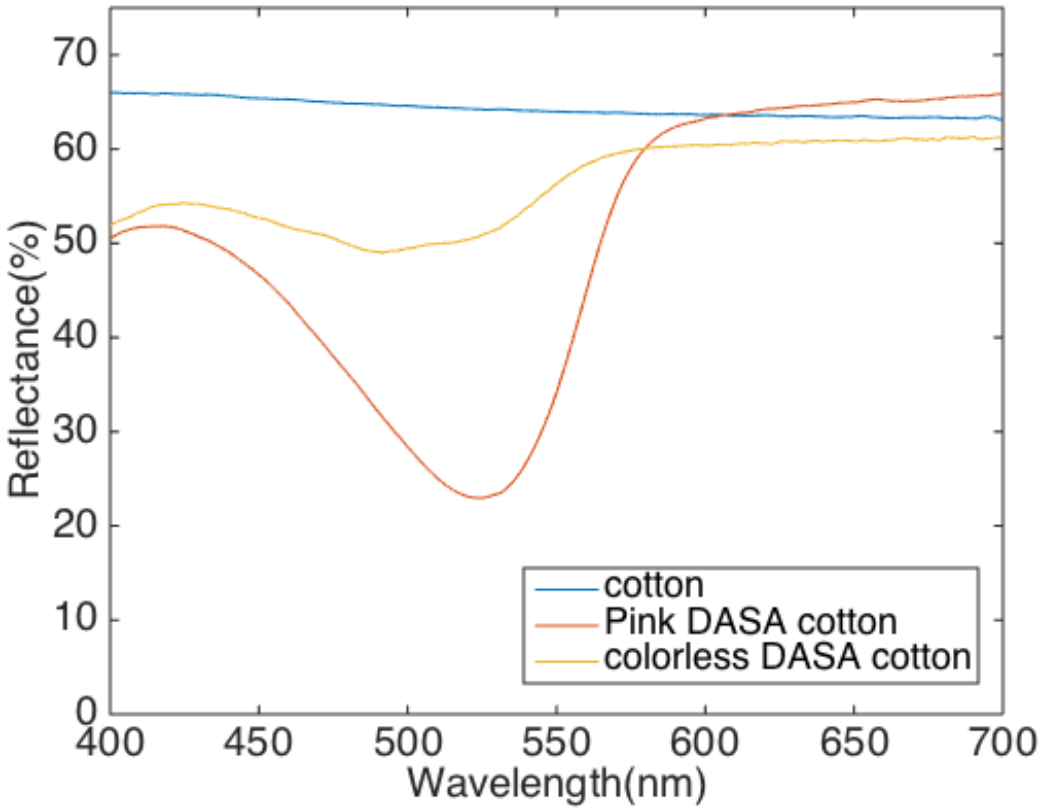


Figure 20 Reflectance of white untreated cotton fabrics, pink DASA cotton fabrics and colorless cotton fabrics

Chapter 3 Possible Application

With the attachment of DASA molecules, cotton fabrics are equipped with many new properties that surpass traditional textile fabrics. First, DASA molecules endow cotton with a bright pink color. Second, cotton fabrics modified with DASA molecules are able to switch from pink to colorless when water is applied and reverse back to pink with heating. In summary, DASA modification gives cotton the ability to respond to water and heat, which are ordinary sources of energy from the surroundings and can be easily used. With these novel properties, cotton fabrics modified with DASA molecules could become an important textile with great potential for uses in our lives.

3.1 Children's toy development

One possible market for the new fabric is use in children's toys. When considering toys, what typically springs to mind are childhood memories of a time when one was carefree and light of heart. One may think back to the nights of sleeping with a little teddy bear or recall the days playing house with Barbie dolls. These are sweet memories of a part of one's life. They are also memories of a time that promoted one's emotional and creative development, without one even being aware of it. Some researchers have found that child's play helps to increase adjustment, improve language abilities, and reduce social and emotional problems during early development.[20] Toys are therefore an important element in children's exploration.

At the beginning of human evolution, hunting tools, wood made chariots, and kitchen instruments could be children' toys.[21] These prototypes of toys from ancient times were

not only for fun; rather, they resembled tools that people relied up on for living. Thus, the label "educational toy" is not a new invention of modern time, but something that has existed since time immemorial.

The invention of the cards, jigsaw puzzles in 1800s enabled the first triumphal march of the educational toy.[22] These toys are mysterious to children and could give them incentive to figure out the answer behind the toys hence building up thought patterns.

There is a considerable literature on educational toys in contemporary society. Nearly half of the papers published between 1970 and 1979 concerning children and toys were about educational toys and how toys play a role in the education of children. In the 1980s, much research focused on the use of educational toys that teach natural science, mathematics, and spatial concepts. This literature shows how people have tried to use toys in children's education to influence various aspects of their development. [23]

With the development of science and technology, smart toys that can respond to, or interact with children became possible. There are three essential purposes of these smart toys: (1) they are able to teach a skill; (2) they can make learning fun; and (3) they engage a child and encourage them to take initiative.[24] In designing toys and thinking about the fabrics that might be used to make them, it is important that toys be suitable for children of various ages, sizes, shapes, fine motor skills, and other physical characteristics and abilities.

3.2 Initiation of design

The first idea that came to my mind was to use these new fabrics to make clothes that will change color upon contact with water, visible light, or heat as that is a cutting-edge topic nowadays. These materials are sometimes called smart textiles or wearable technology. However, for now, we are not able to make large batches of DASA cotton because of the limitations of chemical synthesis. Thus, we became interested in the more doable idea of making small clothes for Barbie dolls instead of normal size clothes for adults.

The Barbie doll is a toy designed mainly for girls. Some have suggested that boys' toys offer a better chance for children to form scientific understanding than girls' toys.[25] They ask, how can the Barbie doll play a role as an instructional tool? First, children can talk to Barbie and act as a teacher and learner simultaneously, thus advancing their language abilities. Second, the Barbie doll is used as a dress model for children to learn to use a sewing machine. Third, while it might seem that Barbie has no relation to the scientific field, we are asking, what if we were to involve a color switchable DASA fabric in one of Barbie's outfits? The color change might trigger the curiosity of children and give them an incentive to ask how this happens and to learn a little bit about chemistry. The merit in choosing to make a Barbie doll suit is twofold: we can produce enough cloth for the small size of doll clothes, and the fancy properties of DASA cotton could be appealing and help children to learn.

3.3 Product development

Gender differentiation occurs in toys' selection for children. The Barbie doll is labeled as a "girl's toy," and the target audience of Barbie is girls from 3-12 years old.[26] The

DASA Barbie's suit being developed will focus on girls from 9-12 years old. The idea of this Barbie suit is to encourage children to be involved in the science and build a basic understanding of the magic of chemistry. Girls from 3-8 may be too young to comprehend the science aspect of the toy. Furthermore, research shows that girls begin to lose interest in science during middle school.[27] Thus, if a toy engages girls in science and helps them to learn and have fun, they could be prepared for future studies.

The DASA modified cotton is pink in color, which is a preferred girls' color. However, unicolor Barbie suit could be bold and unattractive to children. Thus, the Barbie suit prototype had DASA modified cotton as top and a blue fabric as bottom as shown in **Figure 21**.

Figure 21 Left: Original DASA modified cotton made Barbie suit. Right: Barbie suit after exposed to water.

After the development of the DASA Barbie suit, a brochure that explains the magic of this newly invented Barbie suit should accompany the product. The methodology to

fabricate the DASA modified cotton fabrics was stated previously, which can be complicated and tedious for children. The concept of this toy accessory is not to teach children what exactly happens here. Instead, what we want to show is that chemistry enables the color change of the Barbie clothes.

When the Barbie is exposed to water, children could be attracted by the fancy color change phenomenon. They may be curious about this color switch and ask why this happens. The brochure with the product could explain this phenomenon in a more comprehensively way and point out the power of the chemistry. Instead of giving complex chemistry formula, a catchy name of the dye is easier for children to call and remember, like “magic DASA”. The “magic DASA” is afraid of water so when water is sprayed on the clothes the pink color goes away. However, heat could save the color and make it pink again. With the combination of the real product and the notes, children may find chemistry is appealing and become fearless to learn. In the package, a piece of the DASA modified cotton could be included to emphasize the magic of this pink fabric also encourages children to make different style Barbie suit themselves.

Chapter 4 Future work

This research describes one type of photochromic DASA molecule that has been successfully attached to cotton fabrics. This is the first trial to apply DASAs on textiles. The results were good. So this is only the start of work that could be done in the future.

First, there are many derivatives of DASA molecules and they appear to be different in color. Thus, in a future study, a variety of DASA molecules could be used to develop fabrics with different colors. Furthermore, various structures of DASA derivatives might have different sensitivities to visible light and reversibility on different substrates. Therefore, it is important to explore the different properties of many different DASA molecules on materials.

Second, we did our experiments only on cotton, which is the most common textile material. There are many other potential materials, including wool, nylon, and polyester that can be modified. New methodologies of attachment for different types of textile materials could be studied, which would also make it possible to apply this technology in other fields.

Third, at this beginning stage of research, we could only make a limited sample of DASA molecules in a flask. If industrial equipment were involved, modification might be able to be done in a more efficient way.

In conclusion, this thesis shows the potential of the functionalization of textile materials. Textiles that could respond and sense is becoming possible. The attachment of DASAs on

cotton fabrics is only a small entry point of inserting function on the textile materials. From this topic, more possibility of developing “smart textile” could be considered.

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